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㉙ **Rubber composition for reinforcing beads of tyres.**

㉚ A rubber composition suitable for reinforcing beads of tyres, having high hardness, high curability and high ageing resistance, which comprises a rubber component containing 30 to 70% by weight of a butadiene rubber containing syndiotactic crystals, 60 to 75 parts by weight of a carbon black having a specified iodine adsorption number and a specified oil absorption, 1 to 2 parts by weight of sulfur and 2 to 4 parts by weight of a sulfenamide accelerator, respectively, per 100 parts by weight of the rubber component, wherein the total amount of sulfur and the sulfenamide accelerator is from 3 to 5 parts by weight.

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The present invention relates to a rubber composition suitable for reinforcing bead portions of pneumatic tyres, and more particularly to a rubber composition suitable for use in a chafer in the bead portions of heavy duty tyres for auto truck, auto bus and other large vehicles.

Tyres used for trucks, buses and so on are required to have high speed performance because of the spread of superhighways, in addition they must bear greater loads due to the increase of size and load of vehicles. Consequently, rubber compositions used in the chafer disposed in the beads of tyres are required more and more to have high hardness, high durability and high ageing resistance.

Since these types of tyres are recapped and retreaded to replace their tread rubber after the completion of first life, they are required to be particularly free from fault. One fault which makes recap of used tyres impossible is deformation of the bead in a tubed tyre. Bead deformation is a phenomenon in tubes tyres where rubber in the bead is located in a spacing between the wheel rim and a ring, thus resulting in deformation during long term use. Rubber compositions used in chafers in beads of tubed tyres are required to have high hardness, high durability and high ageing resistance in order to prevent occurrence of this phenomenon.

In order to obtain rubber compositions satisfying these properties, it has been practised (1) to specially select the kind of carbon black or to increase the amount of carbon black, (2) to increase the amount of sulfur, or (3) to use an ultra-accelerator TT (tetramethylthiuramdisulfide). However, the use of a large amount of carbon black causes problems in processing as it becomes difficult to conduct milling with good dispersion, and burning takes place due to heat generation resulting from the high loading, and the problem that the crack growth resistance of the rubber is deteriorated.

When a large amount of sulfur is incorporated in a rubber, there arise problem changes in physical properties owing to heat, changes in physical properties with the lapse of time and permanent set (deformation owing to heat) becomes large, and the ageing resistance and resistance to breaks such as cracking are deteriorated.

Since the thiuram ultra-accelerator TT produces nitrosoamine which is a carcinogenic substance and it was found to be a mutagen, its use is being prohibited.

It is also proposed in Japanese Patent Publication Kokoku No 57-20164 to incorporate a syndiotactic-1,2-polybutadiene short fibre into a rubber. However, such a short fibre cannot be uniformly dispersed by application of mechanical force and, therefore, desired physical properties are not obtained by incorporation of only such a short fibre.

It is an object of the present invention to provide a rubber composition suitable for reinforcing beads of tyres and having high hardness, high durability and high ageing resistance.

A further object of the present invention is to provide a rubber composition suitable for use in a chafer in beads of tubed tyres, which is excellent in processability such that it does not cause roll bagging and burning during making, and which is also excellent in hardness, durability and ageing resistance and provides tyres which resist well deformation in the bead, rim-chafing and cracking.

These and other objects of the present invention will become apparent from the description hereinafter.

It has been discovered by the inventors that a rubber composition capable of providing a cured rubber having high hardness, high durability and high ageing resistance with good processability is obtained when a butadiene rubber containing syndiotactic crystals is used with a curing system composed of sulfur and a sulfenamide accelerator, even if the amounts of sulfur and carbon black are suppressed.

In accordance with one aspect of the present invention therefore, there is provided a rubber composition suitable for reinforcing beads of tyres which comprises:

(A) a rubber component containing 30 to 70% by weight of a butadiene rubber containing syndiotactic crystals and 70 to 30% by weight of other diene rubbers, the content of syndiotactic crystals in said butadiene rubber being 6 to 17% by weight,

(B) 60 to 75 parts of a carbon black having an iodine adsorption number of 65 to 130 mg/g and an oil adsorption of 90 to 140 ml/100g,

(C) 1 to 2 parts of sulfur, and

(D) 2 to 4 parts of a sulfenamide accelerator, the total amount of said sulfur (C) and said accelerator (D) being from 3 to 5 parts, where all said parts are parts by weight per 100 parts by weight of the rubber component (A).

The rubber component used in the bead-reinforcing rubber composition of the present invention comprises a butadiene rubber containing syndiotactic crystals. The content of this butadiene rubber in the rubber component is from 30 to 70% by weight, preferably 40 to 60% by weight. When the butadiene rubber content is less than 30% by weight, the hardness and abrasion resistance of cured products obtained from the rubber composition tend to lower. When the butadiene rubber content is more than 70% by weight, the processability of the composition tends to deteriorate because the Mooney viscosity is high and accordingly extrusion and milling become difficult.

The butadiene rubber is typically a cis-1,4-polybutadiene. Preferably, the cis content of cis-1,4-polybutadiene is at least 90%.

The butadiene rubber containing syndiotactic crystals is used with at least one of other known diene rubbers, especially natural rubber, isoprene rubber, styrene-butadiene rubber and butadiene rubber free of syndiotactic crystals.

A representative example of the syndiotactic crystals is a syndiotactic-1,2-polybutadiene in the form of a short fibre.

The content of syndiotactic crystals in the butadiene rubber is from 6 to 17% by weight, preferably 10 to 15% by weight. When the syndiotactic crystal content is less than 6% by weight, the hardness and abrasion resistance tend to lower. When the content is more than 17% by weight, the processability tends to deteriorate.

Preferable examples of the butadiene rubber containing syndiotactic crystals are, for instance, a mixture of a cis-1,4-polybutadiene as a matrix and a syndiotactic-1,2-polybutadiene short fibre dispersed in the matrix, and a block copolymer or graft copolymer of cis-1,4-polybutadiene and syndiotactic-1,2-polybutadiene wherein the syndiotactic-1,2-polybutadiene in the form of a short fibre is block-copolymerised or graft-copolymerised to cis-1,4-polybutadiene.

Such a cis-1,4-polybutadiene containing a crystalline syndiotactic-1,2-polybutadiene in the form of a short fibre is known in the art and is obtained for instance by a method wherein a crystalline syndiotactic-1,2-polybutadiene is mechanically mixed with a matrix cis-1,4-polybutadiene so as to disperse a crystal short fibre into the matrix; or by a two stage polymerisation method wherein cis-polymerisation of butadiene is first conducted and subsequently 1,2-syndiotactic polymerisation of butadiene is conducted in the presence of the produced cis-1,4-polybutadiene so as to produce a block or graft copolymer of cis-1,4-polybutadiene and syndiotactic-1,2-polybutadiene or a mixture of cis-1,4-polybutadiene as a matrix and a crystalline syndiotactic-1,2-polybutadiene short fibre dispersed in the matrix.

In the case of the mechanical mixing method, cis-1,4-polybutadiene containing a crystalline syndiotactic-1,2-polybutadiene short fibre having a maximum diameter of not more than 10  $\mu\text{m}$  and an average diameter of less than 1  $\mu\text{m}$  can be advantageously prepared, for instance, by kneading particles of syndiotactic-1,2-polybutadiene having a particle size of 10 to 700  $\mu\text{m}$  with uncured cis-1,4-polybutadiene at a temperature of not more than 190°C, extruding the obtained mixture at a temperature higher than the melting point of syndiotactic-1,2-polybutadiene by at least 5°C through a circular die having an inner diameter of 1 to 5mm and a length/inner diameter ratio of 1 to 20, cooling the extrudate to room temperature and drawing it by rolls at a roll temperature of 50° to 100°C.

The mixture of cis-1,4-polybutadiene and a short fibre of crystalline syndiotactic-1,2-polybutadiene prepared by the two stage polymerisation method is particularly preferred in the present invention. This mixture is in the form of a composite composed of an elastomer and fibrous crystals. Since in the second stage of polymerisation butadiene is polymerised by stirring in the presence of a syndiotactic polybutadiene polymerisation initiator in a highly viscous solution of a high cis-1,4-polybutadiene produced in the first stage, the syndiotactic-1,2-polybutadiene is produced in a fine fibrous form by the high shearing force and uniformly dispersed in the cis-1,4-polybutadiene matrix. The syndiotactic-1,2-polybutadiene short fibre usually has a diameter of 0.02 to 0.1  $\mu\text{m}$  and a degree of crystallisation of at least 70% or more preferably at least 80%. Such a composite polybutadiene is commercially available under the trade mark "UBEPOL-VCR" from Ube Industries Limited, and UBEPOL-VCR 406, 412 and 617 can be used in the present invention.

The carbon black used in the present invention is one having an iodine adsorption number of 65 to 130mg/g, preferably 75 to 125mg/g, and an oil absorption of 90 to 140 ml/100 g as measured using dibutyl phthalate (DBP). When the iodine adsorption number is less than 65mg/g, the hardness and abrasion resistance tend to be too low, and when the iodine adsorption number is more than 130mg/g, the permanent set under a constant stress and the rate of hardness rise after heat ageing deteriorate too far. When the oil absorption is less than 90 ml/100g, the hardness and abrasion resistance are too low and when the oil absorption is more than 140 ml/100g, the processability deteriorates since the viscosity of the rubber rises.

Examples of such a carbon black are, for instance, N220, N330 and N550 according to ASTM.

The carbon black is used in an amount of 60 to 75 parts by weight per 100 parts by weight of the rubber component. When the amount of carbon black is less than 60 parts by weight, the hardness, abrasion resistance and permanent set under a constant stress deteriorate. When the amount of carbon black is more than 75 parts by weight, the processability is too poor.

Sulfur is used in an amount of 1 to 2 parts by weight per 100 parts by weight of the rubber component. When the amount of sulfur is less than 1 part by weight, the desired hardness is not obtained, and when the amount of sulfur is more than 2 parts by weight, the permanent set under a constant stress and the rate of hardness rise by thermal ageing, are too poor.

It is important to use a specified amount of sulfur with a specified amount of a sulfenamide accelerator.

Known sulfenamide accelerators can be used in the present invention. Examples of the sulfenamide accelerator are, for instance, N-tert-butyl-2-benzothiazolylsulfenamide (TBBS), N-cyclohexyl-2-benzothiazolylsulfenamide (CBS), N-oxydiethylene-2-benzothiazolylsulfenamide (OBS) and N,N-dicyclohexyl-2-benzothiazolylsulfenamide (DZ).

The sulfenamide accelerator is used in an amount of 2 to 4 parts by weight per 100 parts by weight of the rubber component. When the amount of the accelerator is less than 2 parts by weight, the desired hardness is not obtained. When the amount of the accelerator is more than 4 parts by weight, the rubber composition has a tendency to a short scorching time and burning takes place during processing.

It is preferable that the total amount of sulfur and the sulfenamide accelerator is from 3 to 5 parts by weight per 100 parts by weight of the rubber component, and the ratio of sulfenamide accelerator to sulfur is from 1 to 4 by weight. When the total amount is less than 3 parts by weight, the hardness and the durability are lowered. When the total amount is more than 5 parts by weight, the processability (burning) and the permanent set tend to deteriorate. Also, when the accelerator/sulfur ratio is less than 1, the rate of hardness rise by thermal ageing tends to increase, and when the accelerator/sulfur ratio is more than 4, the composition has a tendency for the scorching time to be too short and burning takes place during processing.

The rubber composition of the present invention may contain other additives for rubbers generally used in the production of tyres, for example, antioxidant, softener, activator such as zinc oxide or stearic acid, a curing retarder and the like.

From the viewpoint of application to the reinforcement of beads of tyres, it is preferable that the rubber composition of the present invention is such that the cured product obtained from the composition has a JIS A hardness measured at 20°C of at least 75, especially at least 80, and preferably up to 90, a rate of rise in hardness by thermal ageing of at most 10%, especially at most 8%, a permanent set under a constant stress of at most 12%, especially at most 10%, and a picoabrasion index of at least 240, especially at least 250, as measured according to ASTM D 2288. When the JIS A hardness is less than 75, the hardness is insufficient for reducing deformation of a bead. When the rate of rise in hardness by thermal ageing is more than 10%, beads of used tyres have a greatly increased hardness and accordingly recapped tyres would suffer damage such as cracking. When the picoabrasion index is less than 240, the rim chafing characteristic tends to deteriorate.

The term "JIS A hardness" as used herein means a hardness measured at 20°C using an A type hardness tester according to JIS K 6301.

The term "rate of rise in hardness by thermal ageing" as used herein indicates a value calculated according to the equation

$$\text{Rate of hardness rise (\%)} = \frac{q - p}{p} \times 100$$

wherein p is a value of JIS A hardness of a cured product measured at 20°C, and q is a value of JIS A hardness of the cured product measured at 20°C after allowing the cured product to stand in an oven at 100°C for 144 hours.

The terms "permanent set under a constant stress" as used herein indicates a value obtained by putting bench marks of 2cm intervals on a JIS No. 3 dumbbell specimen punched out of a slab of cured rubber composition having a thickness of 2mm, elongating the specimen by a constant stress of 20kgf/cm<sup>2</sup>, allowing it to stand in an oven at 100°C for 2 hours in that state, releasing the stress, allowing the specimen to stand at room temperature for 30 minutes, measuring the distance r between the marks and calculating the permanent set (%) according to the following equation:

$$\text{Permanent set} = \frac{r - 2}{2} \times 100$$

The present invention is more specifically described and explained by means of the following Examples wherein all parts and % are by weight unless otherwise noted. It is to be understood that the present invention is not limited to the Examples.

#### Example 1

Rubber compositions were prepared according to the following recipe using the recipe shown in Table 1 by kneading a rubber, a filler and reagents in a BR type Banbury mixer adding them in that order, and then mixing the mixture with a curing agent (sulfur) and a curing accelerator on 8 inch rolls.

<u>Ingredients</u>	<u>Amount (part)</u>
Rubber	100
Carbon black N220 <sup>*1</sup>	70
Wax	1
Antioxidant RD <sup>2</sup>	2
Stearic acid	2
Zinc oxide	3
Sulfur	1.5
Curing accelerator TBBS <sup>3</sup>	2
Curing retarder PVI <sup>4</sup>	0.3

## (Notes)

\*1 Carbon black N220 (iodine adsorption number 121mg/g, oil absorption 114 ml/100g) made by Showa Cabot Kabushiki Kaisha

\*2 Poly(2,2,4-trimethyl-1,2-dihydroquinone) made by Ouchi Shinko Kagaku Kabushiki Kaisha  
 \*3 N-tert-butyl-2-benzothiazolylsulfenamide made by Ouchi Shinko Kagaku Kabushiki Kaisha  
 \*4 N-cyclohexylthiophthalimide made by Monsanto Kabushiki Kaisha Japan

The Mooney viscosity ( $ML_{1+4}$ ) and scorching time ( $t_{10}$ ) of the rubber composition were measured at 130°C according to JIS K 6300.

The rubber compositions were cured at 150°C for 30 minutes, and the properties of the cured products were measured.

The results are shown in Table 1.

Table 1

Run No	1-1	1-2	1-3	1-4	1-5	1-6
Natural rubber	40	40	40	40	40	40
BR 150B <sup>*1</sup>	60	-	-	-	-	-
VCR <sup>*2</sup> 303	-	60	-	-	-	-
VCR 406	-	-	60	-	-	-
VCR 412	-	-	-	60	-	-
VCR 617	-	-	-	-	60	-
Composite rubber <sup>*3</sup>	-	-	-	-	-	60
Mooney test						
ML <sub>1+4</sub>	70	75	80	88	98	110
t <sub>10</sub>	2	21	21	20	17	15
JIS A hardness						
Before ageing	74	77	78	81	85	87
After ageing (100°C, 144hrs)	80	83	84	88	91	91
Rate of hardness rise (%)	8	8	8	8	7	5
Permanent set (%)	14.0	12.3	10.7	9.9	8.2	7.6
Picoabrasion index	228	238	243	257	268	273

## (Notes)

\*1 Cis-1,4-polybutadiene made by Ube Industries Ltd

\*2 A composite rubber composed of a matrix cis-1,4-polybutadiene (BR) and a fibrous, high crystalline syndiotactic-1,2-polybutadiene (hereinafter referred to as "sPB") dispersed in the matrix, which is commercially available under the trade mark "UBEPOL-VCR" from Ube Industries Ltd and wherein VCR 303 contains 3% of sPB, VCR 406 contains 6% of sPB, VCR 412 contains 12% of sPB and VCR 617 contains 17% of sPB

\*3 A composite rubber composed of the matrix BR and 20% of sPB dispersed in the matrix BR.

The composition of Run Nos. 1-3 to 1-5 have well-balanced good properties such as processability, hardness, durability and ageing resistance and are superior to the compositions of Run Nos. 1-1, 1-2 and 1-6. The composition of Run No. 1-1 is low in hardness and inferior in permanent set under constant stress and abrasion resistance, since a butadiene rubber containing syndiotactic crystals is not used. The composition of Run No. 1-2 wherein a composite rubber containing 3% of sPB is used, is inferior in permanent set under constant stress and abrasion resistance. The composition of Run No. 1-6 is poor in processability because of high Mooney viscosity.

## Example 2

Rubber compositions were prepared in the same manner as in Example 1 according to the following recipe using carbon black shown in Table 2. The rubber compositions were cured at 150°C for 30 minutes.

The properties of the compositions and the cured products are shown in Table 2.

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Ingredients	Amount (part)
Natural rubber	40
UBEPOL-VCR 412	60
Carbon black	70
Wax	1
Antioxidant RD	2
Stearic acid	2
Zinc oxide	3
Sulfur	1.5
Curing accelerator TBBS	2
Curing retarder PVI	0.3

Table 2

Run No	2-1	2-2	2-3	2-4	2-5
<b>Rubber component</b>					
Natural rubber	40	40	40	40	40
VCR 412	60	60	60	60	60
<b>Carbon black*</b>					
N550	70	-	-	-	-
N330	-	70	-	-	-
N220	-	-	70	-	-
N326	-	-	-	-70	-
N110	-	-	-	-	70
<b>Mooney test</b>					
ML <sub>1+4</sub>	68	76	88	73	102
t <sub>10</sub>	26	23	20	25	15
<b>JIS A hardness</b>					
Before ageing	74	78	81	76	85
After ageing (100°C, 144hrs)	80	84	88	81	93
Rate of hardness rise (%)	8	8	8	7	9
Permanent set (%)	12.5	8.8	9.9	12.2	12.4
Picoabrasion index	234	250	257	239	269

**(Notes)**

\* Carbon black made by Showa Cabot Kabushiki Kaisha, the iodine adsorption number and oil absorption of which are as follows:

N550: iodine adsorption number 43mg/g, oil absorption 121 ml/100g  
 N330: iodine adsorption number 82mg/g, oil absorption 102 ml/100g  
 N220: iodine adsorption number 121mg/g, oil absorption 114 ml/100g  
 N326: iodine adsorption number 82mg/g, oil absorption 72 ml/100g  
 N110: iodine adsorption number 145mg/g, oil absorption 113 mg/100g

The compositions of Run Nos. 2-2 and 2-3 have well-balanced good properties and are superior to the compositions of Run Nos. 2-1, 2-4 and 2-5. The composition of Run No. 2-1 is low in hardness and inferior in permanent set and abrasion resistance, since the iodine adsorption number of carbon black used is small. The composition of Run No. 2-4 is inferior in permanent set and abrasion resistance, since the oil absorption of carbon black used is small. The composition of Run No. 2-5 is inferior in permanent set, since the iodine adsorption number of carbon black used is large.

**Example 3**

The procedure of Example 1 was repeated except that a rubber composition was prepared according to the following recipe.



<u>Ingredients</u>	<u>Amount (part)</u>
Natural rubber	40
UBEPOL-VCR 412	60
Carbon black N330*	55
Wax	1
Antioxidant RD	2
Stearic acid	2
Zinc oxide	3
Sulfur	1.5
Curing accelerator TBBS	2
Curing retarder PVI	0.3

## (Notes)

\*N330 iodine adsorption number 82 mg/g, oil absorption 102 ml/100g

The above procedure was repeated except that the amount of carbon black N330 was varied as shown in Table 3.

The results are shown in Table 3.

Table 3

Run No	3-1	3-2	3-3	3-4	3-5	3-6
Rubber component						
Natural rubber	40	40	40	40	40	40
VCR 412	60	60	60	60	60	60
Carbon black N330	55	60	65	70	75	80
Mooney test						
ML <sub>1+4</sub>	62	67	71	76	81	95
t <sub>10</sub>	30	26	25	23	18	14
JIS A hardness						
Before ageing	73	75	77	78	81	84
After ageing (100°C, 144hrs)	77	80	83	84	88	93
Rate of hardness rise (%)	6	7	8	8	9	11
Permanent set (%)	12.7	11.5	9.8	8.8	9.0	11.2
Picoabrasion index	231	240	248	250	253	255

The compositions of Run Nos. 3-2 to 3-5 have well-balanced good properties and are superior to the compositions of Run Nos. 3-1 and 3-6. The composition of Run No. 3-1 containing 55 parts of carbon black is low

in hardness and inferior in permanent set and abrasion resistance. The composition of Run No. 3-6 containing 80 parts of carbon black is inferior in ageing resistance (rate of hardness rise).

#### Example 4

The procedure of Example 1 was repeated except that rubber compositions were prepared according to the following recipe using the rubber shown in Table 4.

The results are shown in Table 4.

<u>Ingredients</u>	<u>Amount (part)</u>
Natural rubber	100
Carbon black N220*	70
Wax	1
Antioxidant RD	2
Stearic acid	2
Zinc oxide	3
Sulfur	1.5
Curing accelerator TBBS	2
Curing retarder PVI	0.5

#### (Notes)

\*N220: iodine adsorption number 121 mg/g, oil absorption 114 mg/100g

Table 4

Run No	4-1	4-2	4-3	4-4	4-5
Rubber component					
Natural rubber	80	60	40	20	50
UBEPOL-VCR 412	20	40	60	80	50
Mooney test					
ML <sub>1+4</sub>	70	78	88	102	82
t <sub>10</sub>	15	18	20	23	19
JIS A hardness					
Before ageing	74	78	81	84	80
After ageing (100°C, 144hrs)	80	84	88	92	86
Rate of hardness rise (%)	8	8	8	9	8
Permanent set (%)	14.5	12.0	9.9	7.6	10.8
Picoabrasion index	230	242	257	267	250

The compositions of Run Nos. 4-2, 4-3 and 4-5 have well-balanced good properties and are superior to

the compositions of Run Nos. 4-1 and 4-4. The composition of Run No. 4-1 wherein a butadiene rubber containing syndiotactic crystals is used in an amount of 20 parts, is inferior in hardness, permanent set and p-coabrasion index. The composition of Run No. 4-4 wherein a butadiene rubber containing syndiotactic crystals is used in an amount of 80 parts, is poor in processability because the Mooney viscosity is too high.

#### Example 5

The procedure of Example 1 was repeated except that a rubber composition was prepared according to the following recipe.

Ingredients	Amount (part)
Natural rubber	40
UBEPOL-VCR 412	60
Carbon black N220*	70
Wax	1
Antioxidant RD	2
Stearic acid	2
Zinc oxide	3
Sulfur	1
Curing accelerator TBBS	1
Curing retarder PVI	0.3

The above procedure was repeated except that the amounts of curing agent (sulfur) and curing accelerator were varied as shown in Table 5.

The results are shown in Table 5.

Table 5

Run No	5-1	5-2	5-3	5-4	5-5	5-6	5-7	5-8	5-9	5-10	5-11	5-12
Natural rubber	40	40	40	40	40	40	40	40	40	40	40	40
UBEPOL-VCR 412	60	60	60	60	60	60	60	60	60	60	60	60
Sulfur	1	1	1	1	1	2	2	2	2	2	3	0.5
Curing accelerator TBBS	1	2	3	4	5	1	2	3	4	5	3	2
Curing retarder PVI	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Mooney test ML <sub>1+4</sub>	87	88	86	85	86	87	85	86	87	88	87	86
t <sub>10</sub>	24	21	18	15	10	22	18	15	13	11	12	23
JIS A hardness												
Before ageing	78	80	82	83	86	82	85	86	88	89	87	77
After ageing (100°C, 144hrs)	86	86	87	87	89	91	92	92	92	93	97	82
Rate of hardness rise (%)	10	8	6	5	4	11	8	7	5	5	11	6
Permanent set (%)	12.3	10.2	9.5	8.9	8.0	12.1	10.0	9.3	8.5	7.6	9.0	11.2
Picoabrasion index	238	250	252	257	255	240	252	256	261	262	257	225

The composition of Run Nos. 5-2 to 5-4, 5-7 and 5-8 have well-balanced good properties and are superior to the compositions of Run Nos. 5-1, 5-5, 5-6 and 5-9 to 5-12. The composition of Run No. 5-1 containing 1

part of sulfur and 1 part of the sulfenamide accelerator TBBS is inferior in permanent set and abrasion resistance. The compositions of Run Nos. 5-5 and 5-10 containing 5 parts of the sulfenamide accelerator TBBS are poor in processability because the scorching time is short and burning is easy to occur. The composition of Run No. 5-6 containing 2 parts of sulfur and 1 part of the sulfenamide accelerator TBBS is inferior in permanent set. The composition of Run No. 5-9 containing sulfur and sulfenamide accelerator in a total amount of 6 parts is inferior in processability because the scorching time is short and burning is easy to occur. The composition of Run No. 5-11 containing 3 parts of sulfur is inferior in rate of hardness rise. The composition of Run No. 5-12 containing 0.5 part of sulfur is inferior in picoabrasion index.

#### Example 6

The processability of the compositions of Run Nos. 1-1, 1-4, 106, 205 and 5-4 obtained in Examples 1, 2 and 5 was estimated according to the following methods.

The results are shown in Table 6.

#### Roll bagging characteristic

Ingredients for a rubber composition were kneaded by a BR type Banbury mixer, and the mixture was formed into a sheet having a thickness of 2mm. The sheet was milled on a mixing mill at a roll temperature of 60°C and at a forward rotation speed of 20rpm and a backward rotation speed of 19rpm and the workability till the sheet was wound on 8 inch rolls was estimated.

The workability of the composition of Run No. 1-1 was estimated as "slightly bad", and the workability of other compositions were relatively estimated comparing with the workability of the composition of Run No. 1-1.

#### Burning

After kneading a rubber composition, it was milled by 8 inch rolls at a roll temperature of 120°C for 5 minutes and the occurrence of burning was observed.

Table 6

Run No. Of the composition used	1-1	1-4	1-6	2-5	54-
Roll bagging characteristic	slightly bad	good	good	good	good
Burning	none	none	slight burning	burning	none

#### Example 7

Tyres (10.00R20, SP540) were prepared using a chafer prepared from each of the rubber compositions of Run Nos. 1-1, 1-4, 2-1, 5-1, 5-8, 5-6 and 5-12. The tyres were fitted to a truck and subjected to a 100,000km practical running test and estimated with respect to degree of deformation, rim chafing and chipping as follows.

The results are shown in Table 7.

#### Degree of deformation of bead base

A wheel rim was detached, and the size (mm) of the protuberance produced by deformation of the bead base located below the bead core, namely the height of the protuberance between the top of the protuberance and the bottom of the bead base was measured and estimated according to the following rating.

A: The size of deformation is less than 1mm.

B: The size of deformation is from 1 to 5mm

C: The size of deformation is more than 5mm.

The size of the deformation for the composition of Run No. 1-1 was 3mm.

Rim Chafing

A wheel rim was detached and the degree of chafing of rubber at the surface contacting the rim flange was visually estimated.

The result for the composition of Run No. 7-1 was regarded as B, and the estimation was, made for the other in three ratings A,B and C wherein:

A indicates the state that a scratch or the like owing to chafing of the bead rubber on the rim flange is slightly observed at the contacting surface;

B indicates the state where the bead rubber sinks or is scratched at a part of the contacting surface owing to chafing with the rim flange; and

C indicates the state where the bead rubber sinks at the contacting surface owing to chafing with the rim flange.

Cracking

After detaching a wheel rim, the whole of the bead was visually observed with respect to the degree of cracking.

Table 7

Run No. of the composition used	1-1	1-4	2-1	5-1	5-8	5-6	7-7
Degree of deformation	B	A	B	B	A	C	A
Rim chafing	B	A	B	B	A	B	C
Cracking	none	none	none	none	none	slightly cracking	none

The rubber compositions of Run Nos. 1-4 and 5-8 according to the present invention only showed a slight deformation and a slight rim chafing, and also did not cause cracking.

In addition to the ingredients used in the Examples, other ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

Claims

1. A rubber composition suitable for reinforcing beads of tyres characterised by
  - (A) a rubber component containing 30 to 70% by weight of a butadiene rubber containing syndiotactic crystals and 70 to 30% by weight of other diene rubbers, the content of syndiotactic crystals in said butadiene rubber being 6 to 17% by weight;
  - (B) 60 to 75 parts of a carbon black having an iodine adsorption number of 65 to 130mg/g and an oil absorption of 90 to 140 ml/100g;
  - (C) 1 to 2 parts of sulfur; and
  - (D) 2 to 4 parts of a sulfenamide accelerator, the total amount of said sulfur (C) and said accelerator (D) being from 3 to 5 parts, and said parts all being parts by weight per 100 parts by weight of said rubber component (A).
2. The composition of claim 1, characterised in that said butadiene rubber containing syndiotactic crystals is a mixture of a matrix cis-1,4-polybutadiene and a fibrous crystalline syndiotactic-1,2-polybutadiene dispersed in the matrix.
3. The composition of claim 2, characterised in that said mixture is a product prepared by a two stage polymerisation of butadiene in which butadiene is polymerised first by a cis-polymerisation and subsequently polymerised in the same system by a 1,2-syndiotactic-polymerisation.
4. The composition of claim 1, characterised in that said butadiene rubber containing syndiotactic crystals is a block or graft copolymer of a cis-1,4-polybutadiene and a crystalline syndiotactic-1,2-polybutadiene.
5. The composition of any of claims 1 to 4, characterised in that the content of said butadiene rubber containing syndiotactic crystals in said rubber component is from 40 to 60% by weight.

6. The composition of any of claims 1 to 5, characterised in that said carbon black has an iodine adsorption number of 75 to 125 mg/g.
7. The composition of any of claims 1 to 6, characterised in that the ratio of said sulfenamide accelerator to said sulfur is from 1 to 4 by weight.
8. The composition of any of claims 1 to 7, characterised in that said sulfenamide accelerator is at least one member selected from the group consisting of N-tert-butyl-2-benzothiazolylsulfenamide, N-cyclohexyl-2-benzothiazolylsulfenamide, N-oxydiethylene-2-benzothiazolylsulfenamide and N,N-dicyclohexyl-2-benzothiazolylsulfenamide.
9. The composition of any of claims 1 to 8, characterised in that said other diene rubber is at least one member selected from the group consisting of natural rubber, isoprene rubber and a butadiene rubber containing no syndiotactic crystals.
10. The composition of any of claims 1 to 9, characterised by a JIS A hardness of at least 75, a rate of rise in hardness by thermal again of at most 10%, a permanent set under a constant stress 20kgf/cm<sup>2</sup> of at most 12% and a picoabrasion index of at least 240 measured according to ASTM D 2288.
11. An automobile tyre characterised by a chafer prepared from the rubber composition of any of claims 1 to 10.



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 7091

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE-A-37 37 595 (BRIDGESTONE CORP.) * claims; examples *	1	C08L9/00 B60C15/06
A	CHIMICAL ABSTRACTS, vol. 97, no. 22, 29 November 1982, Columbus, Ohio, US; abstract no. 183796, * abstract *	1	
D	& JP-B-57 020 164 (BRIDGESTONE TIRE CO.) 27 April 1982		
A	EP-A-0 517 537 (BRIDGESTONE CORP.) * abstract * * claim 1; examples *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08L B60C
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>23 January 1995</b>	Examiner <b>Van Humbeeck, F</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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